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(54) Laser Recording Medium

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(72) Inventor: Akira MORINAKA
c/o NIPPON TELEGR & TELEPH CORP
IBARAKI ELECTRICAL COMMUNICATION LAB
162 Shirane, Aza, Shirakata, Oaza,
Tokai-mura, Naka-gun, Ibaraki

(72) Inventor: Shigeru OIKAWA
c/o NIPPON TELEGR & TELEPH CORP
IBARAKI ELECTRICAL COMMUNICATION LAB
162 Shirane, Aza, Shirakata, Oaza,
Tokai-mura, Naka-gun, Ibaraki

(72) Inventor: Hironori YAMAZAKI
c/o NIPPON TELEGR & TELEPH CORP
IBARAKI ELECTRICAL COMMUNICATION LAB
162 Shirane, Aza, Shirakata, Oaza,
Tokai-mura, Naka-gun, Ibaraki

(72) Inventor: Koji SATO
c/o NIPPON TELEGR & TELEPH CORP
IBARAKI ELECTRICAL COMMUNICATION LAB
162 Shirane, Aza, Shirakata, Oaza,
Tokai-mura, Naka-gun, Ibaraki

(71) Applicant: NIPPON TELEGR & TELEPH CORP

(74) Representative: Patent Attorney Hiroshi NAKAMOTO; others: 01

Specification

1. Title of the Invention Laser Recording Medium

2. Scope of Patent Claims

1. A laser recording medium, comprising two thin films that are transparent to recording light on a substrate; and a light absorber layer absorbing recording light, which is arranged between the two thin films, wherein a plurality of the light absorber layers absorbing recording light are laminated without changing.

2. The laser recording medium according to claim 1, wherein a thin film of SiO_2, TeO_2, WO_3, leuco dye, phenolphthalein, thymolpythalein, a mixture of fatty acid amide and a bisphenol-based compound, or fluoresceine is used as the thin film that is transparent to recording light.

3. The laser recording medium according to claim 1 or 2, wherein, as the light absorber layer absorbing recording light, a semimetal such as tellurium, bismuth, or selenium, a vapor deposited thin film of a metal such as silver or gold, or a layer of vanadyl phthalocyanine, aluminum phthalocyanine, squarylium dye, nickel dithiolene complex, platinum dithiolene complex, or tellurium oxide is used for a semiconductor laser diode, a layer of fluoresceine, rhodamine B, rhodamine 6G, chalcogenide glass, or amorphous silicon including hydrogen is used for an argon laser, or a layer of oxazine-perchlorate, Nile blue A perchlorate, or gallocyanine is used for a helium-neon laser.

4. A laser recording medium, comprising two thin films that are transparent to recording light on a substrate; and a light absorber layer absorbing recording light, which is arranged between the two thin films; wherein a multilayer laser recording medium includes two or more light absorber layers of the same kind and thin films sandwiching the light absorber layers and transparent to recording light; and wherein the multilayer laser recording medium includes two or more light absorber layers of a different kind from the above-mentioned light absorber layers and thin films sandwiching the light absorber layers and transparent to recording light.

5. The laser recording medium according to claim 4, wherein a thin film of SiO_2, TeO_2, WO_3, leuco dye, phenolphthalein, thymolpythalein, a mixture of fatty acid amide and a bisphenol-based compound, or fluoresceine is used as the thin films transparent to recording light.

6. The laser recording medium according to claim 4 or 5, wherein, as the light absorber layer absorbing recording light, a semimetal such as tellurium, bismuth, or selenium, a vapor deposited thin film of a metal such as silver or gold, or a layer of vanadyl phthalocyanine, aluminum phthalocyanine, squarylium dye, nickel dithiolene complex, platinum dithiolene complex, or tellurium oxide is used for a semiconductor laser diode, a layer of fluoresceine, rhodamine B, rhodamine 6G, chalcogenide glass, or amorphous silicon including hydrogen is used for an argon laser, or a layer of oxazine-perchlorate, Nile blue A perchlorate, or gallocyanine is used for a helium-neon laser.

3. Detailed Description of the Invention

[Field of the Invention]

The present invention relates to a laser recording medium that records and reproduces an optical signal by irradiating a laser beam on thin films that are laminated on top of a substrate so as to change a reflection coefficient or a transmissivity thereof.

[Description of the Related Art]

Heat mode recording systems in which a heat effect generated by a laser beam is used for recording are characterized in that,

(1) an excellent recording preservability that does not change over the years is provided,

(2) real time recording and reproduction are possible, and

(3) their recording density is extremely high compared with that of a magnetic recording or the like.

Therefore, applications of the heat mode recording systems for mass storage systems or image files have been widely examined. Conventionally, as a heat mode type recording medium, laser recording materials such as a recording layer formed on a substrate, in which a dye serving as a light absorber is dissolved by an applied binder layer (US Patent No. 1,117,419), or a recording layer in which a layer of a metal, metallic oxide, or chalcogenide is vapor deposited to form a thin film, using a method for forming a thin film such as sputtering (for example, see M. L. Veven, Records of the 11th Symposium on Electron Ion and Beam Technology (1969), Electronics, March 18, p.50 (1968), JP S50-469317A, or the like) are used.

However, the laser recording materials described above are materials that are absorptive at an Ar or He-Ne laser emission wavelength and a recording threshold energy is high in either material, so that it is necessary to use a laser light source whose output is high and a bulky modulator.

Recently, in order to downsize the light source and to make the modulator faster and smaller, a semiconductor laser diode (LD) came to be used for laser recording and a heat mode recording material that uses an emission wavelength of LDs oscillating in the near-infrared region (up to 830 nm) began to be reported (see Yamazaki et. al. in proceedings of a presentation at the autumn annual meeting of the Japan Society of Applied Physics, 17P-H-16, (1980), for example).

However, when a light absorber layer of the recording medium is made of a single metal, it is impossible to prevent oxidation and deterioration from the surface and the recording sensitivity changes over time.

Therefore, there is a need for a medium whose preservation stability is excellent and whose recording threshold is low.

On the other hand, as a method for further improving the recording density, (1) miniaturizing the recording pits and (2) multilayer recording can be considered. However, as for (1), the radius of the recording pits has

reached 1 μm, which is in the wavelength order, at the present state and is difficult to improve drastically . Therefore, (2) multilayer recording is the only method for increasing the recording density. However, such a heat mode recording material for multilayer recording has not been reported so far and an invention of a laser recording medium that is capable of high density recording is awaited.

[Object of the Invention]

The present invention relates to a laser recording medium that utilizes a change in a material state by using light energy of a laser light for recording. An object of the present invention is to provide a laser recording medium having a sensitivity that is the same as or superior to that of a conventional laser recording medium, and being capable of multilayer recording.

[Configuration of the Invention]

That is, the present invention will be described as follows. A first invention of the present invention is an invention of a laser recording medium including two thin films that are transparent to recording light on a substrate; and a light absorber layer absorbing recording light, which is arranged between the two thin films, wherein a plurality of the light absorber layers absorbing recording light are laminated without changing.

A second invention of the present invention is an invention of another laser recording medium, comprising two thin films that are transparent to recording light on a substrate; and a light absorber layer absorbing recording light, which is arranged between the two thin films; wherein a multilayer laser recording medium includes two or more light absorber layers of the same kind and thin films sandwiching the light absorber layers and transparent to recording light; and wherein the multilayer laser recording medium includes two or more light absorber layers of a different kind from

the above-mentioned light absorber layers and thin films sandwiching the light absorber layers and transparent to recording light.

FIG. 1 is a cross-sectional schematic view illustrating a basic configuration of a laser recording medium according to the present invention. In FIG. 1, reference numbers 11 and 13 denote transparent vapor-deposited films, 12 denotes a light absorber layer, and 14 denotes a substrate.

Recording onto this laser recording medium is performed as shown in FIG. 2.

That is, FIG. 2 shows cross-sectional schematic views illustrating examples of a basic recording mechanism of a laser recoding medium according to the present invention. In FIG. 2, reference number 21 denotes a substrate, 22 and 23 denote transparent thin films, 24, 25, and 26 denote light absorber layers, and 27, 28, and 29 denote recording pits.

In the light absorber layer 24 of a heat deformation type, when laser light is irradiated from the side of the transparent substrate 21 or from the side of the thin film 23, the laser light is absorbed by the light absorber layer 24 and is converted into heat energy, then the light absorber layer 24 is dissolved and evaporated, and its reflection coefficient is decreased at the recording pit portion 27 (FIG. 2(A)).

When using the light absorber layer 25 of another heat deformation type, the light absorber layer 25 is swelled and deformed to form the recording pit 28 by heat of laser light in a similar manner, so that its reflection coefficient is increased. (FIG. 2(B)).

When using the light absorber layer 26 of a denaturation type, heat of laser light similarly causes a change in the reflection coefficient of the light absorber layer 26 through crystallization or photochromism or the like, so that the recording pit shown as reference number 29 is formed (FIG. 2(C)).

FIG. 3 is a cross-sectional schematic view illustrating an example of a multilayer laser recording medium according to the present invention. In FIG. 3, reference numbers 30, 32, and 34 denote transparent vapor-deposited

films, 31 and 33 denote light absorber layers of the same kind, 35 denotes a substrate, B denotes a beam for writing, and L denotes a focal lens.

The recording principle of this laser recording medium is similar to that of the medium in FIG. 1, however a selection between the light absorber layers 31 and 33 is performed by changing a focus position of a laser beam, for example. In FIG. 3, beams B_1 and B_2 have a light source with the same wavelength, however the beams can be focused only onto a corresponding light absorber layer to perform recording through lenses L_1 and L_2 whose focus positions are different from each other .

The above figures show only light absorber layers with one layer and two layers, however, it is possible to use three or more layers since the layers are substantially independent from each other.

FIG. 4 shows calculation results of an energy density at layers of a laser recording medium using laminated light absorber layers of the same kind, taking the transmissivity of the light absorber layers and the numerical aperture (NA) of the lenses as parameters. In other words, FIG. 4 shows a degree of interference to other layers when the lens is focused on a certain light absorber layer. That is to say, FIG. 4 is a graph illustrating a relation between a number of the light absorber layers (n) (shown on the horizontal axis) and a power density that reaches the light absorber layers (absolute value) (shown on the vertical axis). In FIG. 4, reference symbol L indicates the thickness of one layer and T indicates the transmissivity of one layer.

As FIG. 4 shows clearly, in a medium using a lens whose NA is 0.5 and a light absorber layer whose transmissivity is 10%, the energy density of the irradiated laser light becomes one tenth or less at a light absorber layer that is separated from a focus point by a distance of 2 μm, and is sufficiently capable of separated recording, that is multilayer recording when considering the recording threshold of the laser recording medium. Stating it succinctly, it is possible to make a laser recording medium by laminating

ten layers of light absorber layers when their transmissivity is 10% and the transparent thin films between the light absorber layers have a thickness of 2 μm or more.

This is a result when light absorber layers of the same kind are used. When light absorber layers with different materials are used, multilayer recording is not affected at all even when thin films between the light absorber layers are 2 μm or less since laser light sources with different wavelengths are used.

Thus, a laser recording medium such as shown in FIG. 5 can be manufactured. That is, FIG. 5 is a cross-sectional schematic view illustrating another example of a laser recording medium according to the present invention. In FIG. 5, reference number 50 denotes a substrate, 51, 53, 54, 55, and 56 denote transparent thin films.

Reference numbers 52 and 57 denote light absorber layers with mutually different characteristic absorbing bands.

Reference number B_1 denotes a recording light source having a wavelength that is absorbed only by the light absorber layer 57, B_2 denotes a recording light source having a wavelength that is absorbed only by the light absorber layer 52.

As described above, it is necessary to separate each pair of light absorber layers 52 or 57 by a distance of 2 μm or more (when NA = 0.5 and T% = 10%) in multilayer recording using light absorber layers of the same kind, however, with a configuration of a laser recording medium as shown in FIG. 5, the light absorber layers 52 and 57 are combined, so that the thickness of the medium becomes small. Furthermore, since the light absorber layers 52 and 57 do not absorb light B_1 or B_2 of the other wavelength, it becomes possible to drastically improve multilayer recording without decreasing the light usage efficacy or affecting the sensitivity.

In the present invention, as an example of the thin film that is transparent to recording light, a thin film of SiO_2, TeO_2, WO_3, leuco dye,

phenolphthalein, thymolpythalein, a mixture of fatty acid amide and a bisphenol-based compound, or fluoresceine can be used.

In the invention, as an example of the light absorber layer absorbing recording light, a semimetal such as tellurium, bismuth, or selenium, a vapor deposited thin film of a metal such as silver or gold, or a layer of vanadyl phthalocyanine, aluminum phthalocyanine, squarylium dye, nickel dithiolene complex, platinum dithiolene complex, or tellurium oxide can be used for a semiconductor laser diode, a layer of fluoresceine, rhodamine B, rhodamine 6G, chalcogenide glass, or amorphous silicon including hydrogen can be used for an Ar laser, or a layer of oxazine-perchlorate, Nile blue A perchlorate, or gallocyanine can be used for a He-Ne laser.

[Working Examples]

Hereinafter, the present invention will be described further in detail with reference to the following Working Examples. However, the invention is not limited to this.

Working Example 1

A mixture of bisphenol A and stearamide in the proportion of 1 to 1 was vapor deposited with an internal pressure of a vacuum chamber that was not more than 1×10^{-5}, at a vapor deposition speed of 10 Å/sec, to a film thickness of 5000 Å, on top of a glass substrate, so that a transparent thin film was formed. Next, Te was vapor deposited to a film thickness of 150 Å on top of the thin film, then crystal violet lactone (hereinafter abbreviated as CVL) was immediately vapor deposited to a film thickness of 1 μm on top of the Te thin film under similar vapor depositing conditions as for the stearamide, and thus a laser recording medium was manufactured. This laser recording medium was constituted by thin films turning transmitted light into a light brown color.

When writing onto this laser recording medium with semiconductor

laser diode (wavelength 830nm) pulses whose light beam radius was 1.5×1.8 μm and whose power at a medium surface was 6.0 mW, recording pits were formed on the medium surface by the heat of the laser light. The pulse width that was necessary to form pits became to have a recording threshold of 100 nsec, which corresponded to a sensitivity of about 30 mJ/cm^2. The reflection coefficient and the transmissivity of the medium changed by the formation of the pits, and existence or nonexistence of a signal record was confirmed by scanning with laser light whose power was decreased.

Working Example 2

A phenolphthalein (hereinafter abbreviated as PP) layer was vacuum deposited to a thickness of 1 μm on top of a polymethyl methacrylate (hereinafter abbreviated as PMMA) substrate, forming a transparent thin film. Next, vanadyl phthalocyanine (hereinafter abbreviated as V-Pc) was vapor deposited to a thickness of 400Å, forming a light absorber layer. Malachite green lactone (hereinafter abbreviated as MGL) was vapor deposited to a thickness of 1 μm on top of the light absorber layer, and thus a laser recording medium was manufactured. This laser recording medium was constituted by thin films turning transmitted light into a light blue color. When writing onto this laser recording medium with a similar laser light as that in the Working Example 1, recording pits were formed at a laser pulse width of 300 nsec. This value corresponded to a sensitivity value of about 100 mJ/cm^2.

Working Example 3

Thymolpythalein (hereinafter abbreviated as TP) was vapor deposited to a thickness of 1.0 μm on top of a polycarbonate (hereinafter abbreviated as PC) substrate, so that a transparent thin film was formed. Subsequently, Bi was vapor deposited to a thickness of 120Å on top of this thin film, then TH-107 (produced by Hodogaya Chemical Co,.Ltd.) was vapor

deposited to a thickness of 5.0 μm. Bi was vapor deposited to a thickness of 100Å on top of this thin film, and lastly CVL was vapor deposited to a thickness of 1.0 μm, and thus a laser recording medium of a double recording type was manufactured.

A laser recording focus was adjusted on the first Bi layer from the medium surface of this laser recording medium, and recording onto the first layer was performed. Subsequently, a recording focus was adjusted on the second Bi layer from the medium surface, and recording onto the second layer was performed. In both cases, when the laser power was decreased to one tenth and the focus was adjusted on the corresponding Bi layer, it was confirmed that recording was performed through which recording pits were formed and the reflection coefficient was decreased. The laser pulse width showed a recording threshold at a laser pulse width of 150 nsec under similar conditions as that of the Working Examples 1 and 2. This value corresponded to a sensitivity of 45 mJ/cm^2.

Working Example 4

CVL was vacuum deposited to a thickness of 2.5 μm on top of a glass substrate, so that a thin film was formed. Next, Te was sputtered to a thickness of 100Å, so that a thin film serving as a light recording layer was formed. Subsequently the sputtering target was changed to SiO_2 and SiO_2 was sputtered to a film thickness of 2000Å, and thus a laser recoding medium was manufactured.

When a semiconductor laser diode light was irradiated on this laser recording medium under the same conditions as those of the Working Examples 1 and 2, it was possible to perform recording at a laser pulse width of 160 nsec. This value corresponded to a sensitivity of 48 mJ/cm^2.

Working Example 5 to 9

Hereinafter, laser recording media as shown in Table 1 were

manufactured and the formation of recording pits was confirmed in performing laser recording. The recording sensitivity is shown in Table 1.

Table 1

Example Number	Medium Configuration	Recording Sensitivity		
	Substrate	First layer	Second layer	Third layer
5	PMMA // CVL / Au / PP / Ag / MGL (1.0 μm) (100 Å) (5.0 μm) (100 Å) (1.0 μm)	150 nsec (45 mJ/cm^2)	180 nsec (60 mJ/cm^2)	—
6	Glass // TH-107 / Al-Pc / SiO_2 / V-Pc / RED-DCF (1.0 μm) (400 Å) (1000 Å) (400 Å) (1.0 μm)	300 nsec (100 mJ/cm^2)	350 nsec (110 mJ/cm^2)	—
7	PC // PP / Ag / CVL / Ag / PP / Ag / CVL (1.0 μm) (100 Å) (2.0 μm) (100 Å) (2.0 μm) (90 Å) (1.0 μm)	150 nsec (45 mJ/cm^2)	200 nsec (60 mJ/cm^2)	200 nsec (60 mJ/cm^2)
8	PMMA // TP / Te / MGL / Al-Pc / TeO_2 / SQ-N / CVL (1.0 μm) (100 Å) (2.0 μm) (400 Å) (3000 Å) (400 Å) (1.0 μm)	200 nsec (60 mJ/cm^2)	250 nsec (75 mJ/cm^2)	200 nsec (60 mJ/cm^2)
9	PMMA // PP / Te / WO_3 / V-Pc / CVL (1.0 μm) (100 Å) (2.0 μm) (400 Å) (2.0 μm)	200 nsec (60 mJ/cm^2)	250 nsec (75 mJ/cm^2)	

Al-Pc: aluminum phthalocyanine, SQ-N: dimethylaminonaphthylsquarylium
RED-DCF: produced by Hodogaya Chemical Co,.Ltd.

Working Example 10

CVL was vapor deposited to a thickness of 1.0 μm on top of a PMMA substrate, so that a transparent thin film was formed. Subsequently, TeO_2, Te, and Ge were vapor deposited together so as to form $TeO_{1.1}Ge_{0.1}$, and the thin film thereof was laminated to a thickness of 1000 Å. Then, PP was vapor deposited to a thickness of 3.0 μm. Furthermore, $TeO_{1.1}Ge_{0.1}$ was laminated to a thickness of 1000 Å, and lastly CVL was vapor deposited to a thickness of 2.0 μm, and thus a laser medium for double recording was manufactured. Then, the recording medium was treated with heat so as to

be changed from a precipitation state to a crystallized state. The focus was adjusted on the first $TeO_{1.1}Ge_{0.1}$ layer from the medium surface of this laser medium, then the focus was adjusted on the second $TeO_{1.1}Ge_{0.1}$ layer, so that recording was performed.

In both cases, when the laser power was decreased to one tenth and the focus was adjusted on the corresponding $TeO_{1.1}Ge_{0.1}$ layer, it was possible to read out that a reflection coefficient was decreased at the recording pit portions.

A laser pulse width was 200 nsec under similar conditions as those of the Working Examples 1, 2, and 3. This value corresponded to a sensitivity of 60 mJ/cm^2.

When a beam area of laser pulse light for recording was expanded tenfold and $TeO_{1.1}Ge_{0.1}$ layers were scanned with an initial laser power width, both the $TeO_{1.1}Ge_{0.1}$ layers were recrystallized and the recording pits were cleared.

Working Example 11

CVL was vapor deposited to a thickness of 1.0 μm on top of a PMMA substrate, then V-Pc (250 Å), PP (3.0 μm), V-Pc (250 Å), and RED-DCF (3.0 μm) were vapor deposited and laminated, and thus a laser medium for double recording was manufactured.

With a similar method to that of the Working Examples 1, 2, 3, and 10, recording onto two layers was performed. The focus was adjusted on V-Pc, and laser light was recorded.

Recording pits were formed at a laser pulse width of 300 nsec. This value corresponded to a sensitivity of 100 mJ/cm^2.

Subsequently, when the focus was adjusted on the second V-Pc layer and laser light was irradiated, recording pits were formed at a laser pulse width of 350 nsec. This value corresponded to a sensitivity of about 120 mJ/cm^2.

This laser recording medium was manufactured so as to have different emitted colors for recording onto the first layer and the second layer.

After recording onto the layers, red and blue color emissions were confirmed by observation with a microscope. Therefore, independent recording and reproduction are clearly made possible by separating the layers by a distance of 3 μm in a film thickness direction.

Working Example 12

TP was vapor deposited to a thickness of 1.0 μm on top of a PMMA substrate, and amorphous silicon including hydrogen was formed at a film thickness of 1000 Å, using plasma CVD. Next, CVL was vapor deposited to a thickness of 2.0 μm, and on the top thereof, $As_{40}Be_{25}Ge_{10}B_{25}$ was formed at a thickness of 3000 Å, by using RF sputtering.
Furthermore, SiO_2 was deposited to a film thickness of 2000 Å on top of the $As_{40}Be_{25}Ge_{10}B_{25}$, and thus a laser recording medium was manufactured.

When the focus of Ar laser light with a wavelength of 514 nm was adjusted on the amorphous silicon layer to perform recording, the refractive index of the amorphous silicon layer was changed and it was possible to perform recording. Next, when Ar laser light with a wavelength of 455 nm was irradiated only on the $As_{40}Be_{25}Ge_{10}B_{25}$ layer to perform recording, the refractive index of the $As_{40}Be_{25}Ge_{10}B_{25}$ layer was changed and it was possible to perform recording. He-Ne laser light was used to read out the recording light .
When an ultraviolet ray was irradiated from a BiO_2 surface of the laser medium, it was possible to erase the recording only at the first $As_{40}Be_{25}Ge_{10}B_{25}$ layer.

[Effect of the Invention]

As described above, the laser recording medium according to the present invention can be manufactured simply, widely, and uniformly with a method in which vapor deposited layers are laminated on top of a substrate. It should be noted that it is easy to manufacture such a medium even with a

transparent substrate such as a plastic substrate that is likely to be deformed by heat or contorted since the manufacturing conditions do not need to include a process of heating the substrate or the like.

Furthermore, the manufactured laser recording medium is provided with a recording sensitivity and a contrast that are the same as or superior to that of a conventional laser recording material of a heat mode type, and planes of the medium are flat before and after recording since the light absorber layers are sandwiched by transparent thin films, and thus, cover a deformation at pit generation portions that is caused by laser recording. Therefore, multilayer recording as shown in the examples in which a plurality of recording media are combined can be easily performed by selecting a focus depth or a wavelength of a laser for recording.

Furthermore, as for the stability of the medium, the transparent thin film as a component material is extremely stable and has an advantage that a stability of the light absorber layer is improved as well since the upper and lower layers that sandwich the light absorber layer have an adequate effect of antioxidation against a deterioration by oxidation that is caused when using a semimetal such as Te or Bi as a light absorber.

4. Brief Description of the Drawings

FIG. 1 is a cross-sectional schematic view illustrating a basic configuration of a laser recording medium according to the present invention. FIG. 2 shows cross-sectional schematic views illustrating examples of a basic recording mechanism of a laser recoding medium according to the present invention. FIG. 3 is a cross-sectional schematic view illustrating an example of multilayer recording by a laser recording medium according to the invention. FIG. 4 is a graph illustrating a relation between a number of the light absorber layers and a power density of a laser recording medium according to the invention. FIG. 5 is a cross-sectional schematic view illustrating another example of a laser recording medium according to the

present invention.

11, 13, 22, 23, 30, 32, 34, 51, 53, 54, 55, 56,: transparent thin layer, 12, 24, 25, 26, 31, 33, 52, 57,: light absorber layer, 14, 21, 35, 50,: substrate, 27, 28, 29, 36, 37,: recording pit , B: beam for writing, L: focal lens.

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⑫発 明 者　森中彰
茨城県那珂郡東海村大字白方字白根162番地日本電信電話公社茨城電気通信研究所内
⑫発 明 者　及川茂
茨城県那珂郡東海町大字白方字白根162番地日本電信電話公社茨城電気通信研究所内
⑫発 明 者　山崎裕基
茨城県那珂郡東海村大字白方字白根162番地日本電信電話公社茨城電気通信研究所内
⑫発 明 者　佐藤弘次
茨城県那珂郡東海村大字白方字白根162番地日本電信電話公社茨城電気通信研究所内
⑪出 願 人　日本電信電話公社
⑭代 理 人　弁理士　中本宏　外1名

明　細　書

1. 発明の名称　レーザ記録媒体

2. 特許請求の範囲

1. 基板上に、記録光に対して透明な2層の薄膜を設け、記録光を吸収する光吸収剤層をその間に挟んだ構造を持つレーザ記録媒体において、記録光を吸収する光吸収剤層を変えることなく複数組積層したことを特徴とするレーザ記録媒体。

2. 記録光に対して透明な薄膜として、SiO_2、TeO_2、WO_3、ロイコ染料、フエノールフタレイン、チモールフタレイン、脂肪酸アミドとビスフエノール系化合物との混合物、又はフルオレセインの薄膜を用いる特許請求の範囲第1項に記載のレーザ記録媒体。

3. 記録光を吸収する光吸収剤層として、半導体レーザ用に、テルル、ビスマス、セレン等の半金属若しくは銀、金等の金属のいずれかの蒸着薄膜、バナジルフタロシアニン、アルミニウムフタロシアニン、スクアリリウム色素、ニツケルジチオレート錯体、白金ジチオレート錯体、又はテルル酸化物の層、アルゴンレーザ用にフルオレセイン、ローダミンB、ローダミン6G、カルコゲナイドガラス、又は水素含有非晶質シリコンの層、ヘリウム−ネオンレーザ用にオキサジン−過塩素酸塩、ナイルブルーA過塩素酸塩又はガロシアニンの層を用いる特許請求の範囲第1項又は第2項に記載のレーザ記録媒体。

4. 基板上に、記録光に対して透明な2層の薄膜を設け、記録光を吸収する光吸収剤層をその間に挟んだ構造を持つレーザ記録媒体において、同一種2つ以上の光吸収剤層とそれを挟んだ記録光に透明な薄膜とでなる多重レーザ記録媒体内に、前記光吸収剤層とは異種の2つ以上の光吸収剤層とそれを挟んだ記録光に透明な薄膜とでなる多重レーザ記録媒体を合せ持つことを特徴とするレーザ記録媒体。

5. 記録光に対して透明な薄膜として、SiO_2、TeO_2、WO_3、ロイコ染料、フエノールフタレイ

ン、チモールフタレイン、脂肪酸アミドとビスフエノール系化合物との混合物、又はフルオレセインの薄膜を用いる特許請求の範囲第4項に記載のレーザ記録媒体。

6. 記録光を吸収する光吸収剤層として、半導体レーザ用に、テルル、ビスマス、セレン等の半金属若しくは銀、金等の金属のいずれかの蒸着薄膜、バナジルフタロシアニン、アルミニウムフタロシアニン、スクアリリウム色素、ニッケルジチオレート錯体、白金ジチオレート錯体、又はテルル酸化物の層、アルゴンレーザ用にフルオレセイン、ローダミンB、ローダミン6G、カルコゲナイドガラス、又は水素含有非晶質シリコンの層、ヘリウム－ネオンレーザ用にオキサジン－過塩素酸塩、ナイルブルーA過塩素酸塩又はガロシアニンの層を用いる特許請求の範囲第4項又は第5項に記載のレーザ記録媒体。

3. 発明の詳細な説明

〔産業上の利用分野〕

本発明は、基板上に積層された薄膜にレーザ・ビームを照射してその反射率、あるいは透過率を変化させることにより、光学的信号を記録再生するレーザ記録媒体に関する。

〔従来技術〕

レーザ・ビームによる熱的効果を記録に利用するヒートモード記録方式は

(1) 経年変化がなく記録保存性が良い。

(2) 実時間で記録、再生ができる。

(3) 記録密度が磁気記録等に比べ非常に高密度である。

といつた特徴を持つため大容量記憶システム、画像ファイルへの応用が幅広く検討されている。従来、ヒートモード形の記録媒体として、基板上に、光吸収剤となる染料とこれを溶解するバインダの塗布層によつて記録層が形成されたもの（米国特許第1117419号明細書）や、金属、金属酸化物、カルコゲナイド層を蒸着、スパッタリング等の薄膜形成法を用いて薄膜化し記録層とするレーザ記録材料が用いられてきた（例えばM.L.ヘーヘン（M.L.Veven）、エレクトロン イオン アンド ビーム テクノロジー（Electron Ion and Beam Technology）第11回シンポジウム記録（1969）、エレクトロニクス（Electronics）（1968）3月18日号50頁、特開昭50－46317号公報等参照）。

しかし、上で述べたレーザ記録材料はアルゴン（Ar）、ヘリウム－ネオン（He-Ne）レーザ発振波長に吸収を持つ物質であつて、しかも、いずれも記録閾値エネルギーが高く、高出力レーザ光源を必要とし、変調器も大型のものを使用せねばならなかつた。

最近、光源の小型化、変調器の高速小型化を目的として、半導体レーザ（LD）がレーザ記録に用いられるようになり、発振波長が近赤外域のLD用（～830 nm）を用いたヒートモード記録材料が報告され始めた（例えば1980年、応用物理学会秋季全国大会講演予稿集、山崎ほか17P－H－16参照）。

しかし、記録媒体の光吸収層が金属単体である場合は、表面からの酸化劣化が防げず、記録感度が経時変化を起す欠点を持つていた。

このために、保存安定性の良い媒体で、かつ記録閾値の低い媒体が望まれている。

他方、記録密度をより向上させる方法としては(1)記録ピットの微細化、(2)記録の多重化が考えられるが、(1)は現段階で記録ピット径は波長オーダの1 μm に達し大幅な向上は困難である。そこで(2)の記録の多重化が唯一の記録の高密度化を図る方法であるが、これまでにこのような記録多重化を目的としたヒートモード記録材料が報告されたことはなく、高密度記録可能なレーザ記録媒体の発明が待ち望まれていた。

〔発明の目的〕

本発明は、レーザ光の光エネルギーを用いて物質の状態変化を記録として利用するレーザ記録媒体に関するものでありその目的は、従来のレーザ記録媒体に比べて同等以上の感度を持ち、かつ多重記録の可能なレーザ記録媒体を提供す

ることにある。

〔発明の構成〕

すなわち、本発明を概説すれば、本発明の第1の発明はレーザ記録媒体の発明であつて、基板上に、記録光に対して透明な2層の薄膜を設け、記録光を吸収する光吸収剤層をその間に挟んだ構造を持つレーザ記録媒体において、記録光を吸収する光吸収剤層を変えることなく複数組積層したことを特徴とする。

そして、本発明の第2の発明は別のレーザ記録媒体の発明であつて、基板上に、記録光に対して透明な2層の薄膜を設け、記録光を吸収する光吸収剤層をその間に挟んだ構造を持つレーザ記録媒体において、同一種2つ以上の光吸収剤層とそれを挟んだ記録光に透明な薄膜とでなる多重レーザ記録媒体内に、前記光吸収剤層とは異種の2つ以上の光吸収剤層とそれを挟んだ記録光に透明な薄膜とでなる多重レーザ記録媒体を合せ持つことを特徴とする。

第1図は、本発明によるレーザ記録媒体の基本構成を示す断面概略図である。第1図中11、13は透明の蒸着膜、12は光吸収剤層、14は基板を各々示している。

このレーザ記録媒体への記録は第2図に示したように行われる。

すなわち第2図は、本発明によるレーザ記録媒体の基本の記録機構の各種の例を示す断面概略図である。第2図中、符号21は基板、22、23は透明な薄膜、24、25、26は光吸収剤層、27、28、29は記録ピットを意味する。

熱変形タイプの光吸収剤層24では21の透明基板側あるいは23の薄膜側からレーザ光が照射されると、24の光吸収剤層に吸収されて熱エネルギーとなり、光吸収剤層24は溶融、蒸発し、記録ピット部27は反射率が低下する〔第2図(A)〕。

他の熱変形タイプの光吸収剤層25を用いると同様なレーザ光の熱により光吸収剤層25が膨張し、変形し、記録ピット28となり反射率が増加する〔第2図(B)〕。

変性タイプの光吸収剤層26を用いると同様なレーザ光の熱により光吸収剤層26は結晶化、あるいはフォトクロミズム等の反射率変化を生じ29で示される記録ピットが生じる〔第2図(C)〕。

第3図には本発明による多重レーザ記録媒体の1例を示す断面概略図である。第3図中30、32、34は透明の蒸着膜、31、33は同一種の光吸収剤層、35は基板、Bは書込用ビーム、Lは焦点レンズを示す。

このレーザ記録媒体の記録原理は第1図の媒体と同様であるが、例えば光吸収剤層31、33の選択はレーザビームの焦点位置を変化させる。第3図中B_1、B_2は同一波長の光源であるが焦点位置の違うL_1、L_2によつて相当する光吸収剤層にのみ結像して記録が行える。

以上は一層、二層の光吸収剤層についてのみ図を記載したが、本質的に各層間が独立しているため三層以上の多重化が可能である。

第4図には、光吸収剤層の透過率とレンズの開口率(NA)をパラメータとした積層形の同一種の光吸収剤層を用いたレーザ記録媒体の各層のエネルギー密度の計算結果を示す。換言すれば、レンズで当該吸収剤層に焦点を絞つたときの他層への干渉の大きさを示す。すなわち第4図は光吸収剤層の番号(n)(横軸)と光吸収剤層に到達するパワー密度(相対値)(縦軸)との関係を示すグラフである。第4図中Lは1層の厚さ、Tは1層の透過率を示す。

第4図から明らかなように、NA=0.5のレンズを用いて透過率10%の光吸収剤層を用いた媒体においては、焦点から2 μm 離れた光吸収剤層では照射レーザ光のエネルギー密度は1/10以下になり、レーザ記録媒体の記録閾値を考えると十分に記録分離が可能、つまり記録の多重が可能である。簡単に述べると10%の透過率の光吸収剤層を10層並べたレーザ記録媒体を作り、光吸収剤層間の透明な薄膜が2 μm 以上あれば10重が可能であることを示している。

これは同一種の光吸収剤層を用いた場合の結果であり、光吸収剤層を異なつた物質にすると、波長の異なるレーザ光源を用いるため光吸収剤層間の透明な薄膜は2 μm 以下であつても多重記録には何ら影響がない。

つまり、第5図に示したようなレーザ記録媒体が構成できる。すなわち、第5図は本発明によるレーザ記録媒体の他の1例を示す断面概略図である。第5図中、50は基板、51、53、54、55、56は透明な薄膜を示す。
52、57は各各互いに特性吸収帯の異なる光吸収剤層を示している。
B_1は光吸収剤層57にのみ吸収される波長の記録光源、B_2は光吸収剤層52にのみ吸収される波長の記録光源とする。

前述のように同一種の光吸収剤層を用いた多重記録において、光吸収剤層52あるいは57の組は各各2 μm (NA=0.5、T%=10%の時)以上離す必要があるが第5図のようにレーザ媒体を構成すると52と57を組合せることによつて媒体厚を小さくすることができる。また、52、57は互いに他波長の光B_1、B_2を吸収しないため、光の利用効率が低下し感度に影響することなく記録の多重度を大幅に向上させることができる。

本発明で用いる記録光に対して透明な薄膜の例としては、SiO_2、TeO_2、WO_3、ロイコ染料、フエノールフタレイン、チモールフタレイン、脂肪酸アミドとビスフエノール系化合物との混合物、又はフルオレセインが挙げられる。

本発明で用いる記録光を吸収する光吸収剤層の例としては、半導体レーザ用に、テルル、ビスマス、セレン等の半金属若しくは銀、金等の金属のいずれかの蒸着薄膜、バナジルフタロシアニン、アルミニウムフタロシアニン、スクアリリウム色素、ニッケルジチオレート錯体、白金ジチオレート錯体、又はテルル酸化物の層、Ar レーザ用にフルオレセイン、ローダミンB、ローダミン6G、カルコゲナイドガラス、又は水素含有非晶質シリコンの層、He-Ne レーザ用にオキサジン-過塩素酸塩、ナイルブルーA過塩素酸塩又はガロシアニンの層が挙げられる。

〔実施例〕

以下、本発明を実施例により、更に具体的に説明するが本発明はこれに限定されない。

実施例1

ガラス基板上に、ビスフエノールAとステアリン酸アミド1対1混合物を真空槽内圧1×10^{-5}トル以下で10Å/sec の蒸着速度で5000Åの膜厚で蒸着し透明な薄膜を作製した。次にこの薄膜上にTe を150Åの膜厚で蒸着し、すぐにこのTe 薄膜上に、クリスタルバイオレットラクトン(以下、CVL と略記する)をステアリン酸アミド蒸着の条件と同様に1 μm の膜厚で蒸着し、レーザ記録媒体を作製した。このレーザ記録媒体は、透過光で薄褐色を呈する薄膜であつた。

このレーザ記録媒体に光ビーム径1.5×1.8 μm 媒体面でのパワー60 mW の半導体レーザ(波長830 nm)パルスで書込みを行うと、記録媒体にレーザ光の熱によつて記録ピットが形成された。ピット形成に必要なパルス幅は100 nsec が記録閾値となり約30 mJ/cm²の感度に相当した。ピット形成により媒体の反射率、透過率が変化しパワーを弱めたレーザ光で走査することにより信号記録の有無が確かめられた。

実施例2

ポリメチルメタクリレート(以下、PMMA と略記する)基板上にフエノールフタレイン(以下、PP と略記する)層を1 μm 真空蒸着して透明な薄膜を作製する。次にバナジルフタロシアニン(以下V-Pc と略記する)を400Å蒸着して光吸収剤層を形成した。光吸収剤層上にマラカイトグリーンラクトン(以下、MGL と略記する)を1 μm 蒸着してレーザ記録媒体とする。このレーザ記録媒体は透過光で薄ブルーを呈する薄膜となつた。このレーザ記録媒体に実施例1と同様のレーザ光を用いて記録を行つたところ、300 nsec のレーザパルス幅で記録

ピットが形成された。感度的には、約100 mJ/cm^2の値に相当する。

実施例3

ポリカーボネート（以下、PCと略記する）基板上に、チモールフタレイン（以下、TPと略記する）を1.0 μm 蒸着して透明薄膜とした。続いてこの薄膜上にBiを120Å蒸着し更にTH-107（保土ケ谷化学社製）を5.0 μm 蒸着した。この薄膜上にBiを100Å蒸着し最後にCVLを1.0 μm の厚さで蒸着して2重記録形のレーザ記録媒体とした。

このレーザ記録媒体に媒体表面から第1層Biにレーザ記録焦点を合せ第1層記録を行つた。続いて媒体表面から第2層Biに焦点を合せ第2層記録を行つた。いずれもレーザパワーを1/10に弱め対応するBi層に焦点を合せることにより、記録ピットが生じて反射率低下した記録が行われたことが確認できた。レーザパルス幅は上記実施例1及び2と同様の条件で、レーザ・パルス幅150 nsecの記録閾値を示した。感度として45 mJ/cm^2に対応していた。

実施例4

ガラス基板上にCVLを2.5 μm 真空蒸着して、薄膜を得た。次にTeを100Åスパッタリングして光記録層薄膜を作製し、続いてスパッタリングターゲットをSiO_2に切替えてSiO_2の2000Åスパッタ膜で覆いレーザ記録媒体とする。

このレーザ記録媒体に、半導体レーザ光で実施例1及び2と同条件で照射を行うとレーザパルス幅160 nsecで記録が行えた。感度として48 mJ/cm^2に対応した。

実施例5～9

以下表1に示したレーザ記録媒体を構成し、レーザ記録を行つて記録ピットの形成を確認した。記録感度を表1に示した。

表 1

実施例番号	媒体構成 基板	媒体構成	記録感度 第1層	記録感度 第2層	記録感度 第3層
5	PMMA /	CVL / Au / PP / Ag / MGL (1.0 μm) (100Å) (5.0 μm) (100Å) (1.0 μm)	150 nsec (45 mJ/cm^2)	180 nsec (60 mJ/cm^2)	——
6	ガラス /	TH-107 / Aℓ-Pc / SiO_2 / V-Pc / RED-DCP (1.0 μm) (400Å) (1000Å) (400Å) (1.0 μm)	300 nsec (100 mJ/cm^2)	350 nsec (110 mJ/cm^2)	——
7	PC /	PP / Ag / CVL / Ag / PP / Ag / CVL (1.0 μm) (100Å) (2.0 μm) (100Å) (2.0 μm) (90Å) (1.0 μm)	150 nsec (45 mJ/cm^2)	200 nsec (60 mJ/cm^2)	200 nsec (60 mJ/cm^2)
8	PMMA /	TP / Te / MGL / Aℓ-Pc / TeO_2 / SQ-N / CVL (1.0 μm) (100Å) (2.0 μm) (400Å) (3000Å) (400Å) (1.0 μm)	200 nsec (60 mJ/cm^2)	250 nsec (75 mJ/cm^2)	200 nsec (60 mJ/cm^2)
9	PMMA /	PP / Te / WO_3 / V-Pc / CVL (1.0 μm) (100Å) (2.0 μm) (400Å) (2.0 μm)	200 nsec (60 mJ/cm^2)	250 nsec (75 mJ/cm^2)	

Aℓ-Pc：アルミニウムフタロシアニン、SQ-N：ジメチルアミノナフチルスクアリリウム

RED-DCP：保土ケ谷化学社製

実施例10

PMMA 基板上に、CVL 1.0 μm 蒸着して透明薄膜を作製した。続いて TeO_2、Te、Ge を共蒸着して、$TeO_{1.1}$ $Ge_{0.1}$ 組成にして薄膜を1000Å積層し、PP を3.0 μm 蒸着し、更に $TeO_{1.1}$ $Ge_{0.1}$ 1000Å積層し、最後に CVL 2.0 μm を蒸着して2層記録レーザ媒体とし、熱処理し析出状態から結晶化状態とした。このレーザ媒体に媒体表面から第1層目 $TeO_{1.1}$ $Ge_{0.1}$ に焦点を合せ続いて、第2層 $TeO_{1.1}$ $Ge_{0.1}$ に焦点を合せ記録を行つた。

いずれもレーザパワーを1/10 に弱め対応する $TeO_{1.1}$ $Ge_{0.1}$ に焦点を合せることにより、記録ピット部の反射率低下が読出せた。

レーザパルス幅は実施例1、2、3と同様の条件で200 nsec で、感度として60 mJ/cm² に対応していた。

いずれの $TeO_{1.1}$ $Ge_{0.1}$ 層も記録用レーザパルス光のビーム面積を10倍に広げ、初期のレーザパワー幅でスキャンすることにより再結晶化して記録ピットは消失した。

実施例11

PMMA 基板上に、CVL 1.0 μm を蒸着して、次に V-Pc 250Å、PP 3.0 μm、V-Pc 250Å、RED-DOF 3.0 μm 蒸着積層して2層記録レーザ媒体を作製した。

実施例1、2、3、及び10と同様な方法で二層書込みを行つた。焦点を V-Pc に合せてレーザ光を記録した。

レーザパルス幅300 nsec で記録ピットが形成された。これは感度として100 mJ/cm² に対応している。

続いて焦点を第2層 V-Pc に合せて、レーザ光を照射すると、レーザパルス幅350 nsec で記録ピットが形成された。これは記録感度として約120 mJ/cm² に対応している。

本レーザ記録媒体は第一層第二層の記録に対して異なつた発色をするように作製したもので各層の記録後、顕微鏡観察で赤、青の発色が確認できた。したがつて膜厚方向3 μm の分離で独立に記録再生が可能なことは明らかである。

実施例12

PMMA 基板上に、TP 1.0 μm を蒸着し、プラズマ CVD 法を用いて水素含有アモルファスシリコンを1000Åの膜厚で作製した。次に CVL を2.0 μm 蒸着しその上に $As_{40}Se_{25}Ge_{10}S_{25}$ を RF スパッタにより3000Å作製した。更に $As_{40}Se_{25}Ge_{10}S_{25}$ 上に SiO_2 を2000Åの膜厚でつけてレーザ記録媒体とした。

波長514 nm の Ar レーザ光をアモルファスシリコン層に焦点を合せ記録を行うと、アモルファスシリコン層の屈折率が変化して記録が行えた。次に波長455 nm の Ar レーザ光を $As_{40}Se_{25}Ge_{10}S_{25}$ 層に絞つて照射し記録を行うと、$As_{40}Se_{25}Ge_{10}S_{25}$ の屈折率が変化して記録が行えた。各各の記録光の読出しには He-Ne レーザ光を用いた。

レーザ媒体の SiO_2 面から紫外光を照射すると第1層の $As_{40}Se_{25}Ge_{10}S_{25}$ の記録のみが消去できた。

〔発明の効果〕

以上説明したように、本発明のレーザ記録媒体は、基板上への蒸着膜積層といつた方法で簡便に広面積にかつ均一に作製できる。また、作製条件は基板加熱といつた過程を通す必要がないためプラスチック基板のような熱変形、ひずみを生じやすい透明基板でも容易に作製が行える。

また、作製されたレーザ記録媒体は、既存のヒートモード型のレーザ記録材料と同等以上の記録感度、コントラストを持ち、かつ光吸収剤層が透明な薄膜でサンドイッチされているために、レーザ記録によるピット生成部の変形がカバーされて媒体は平面が記録前後ともフラットである。したがつて実施例に示したような記録媒体を複数組で組合せるような多重記録が記録用レーザの焦点深度あるいは波長選択によつて容易に行える。

更に、媒体の安定性として、構成材料としての透明な薄膜は極めて安定であると同時に、

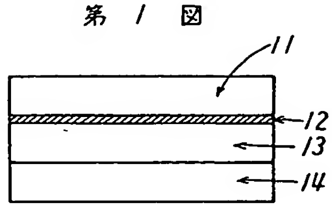
Te、Bi 等の半金属を光吸収剤として用いる際に生じる酸化による劣化に対して上下層のサンドイッチ層が十分酸化防止効果を持つため光吸収剤層の安定性も向上する利点を持つている。

4.図面の簡単な説明

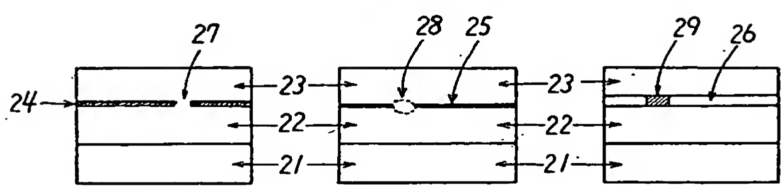
第1図は本発明によるレーザ記録媒体の基本構成を示す断面概略図、第2図は本発明によるレーザ記録媒体の基本の記録機構の各種の例を示す断面概略図、第3図は本発明によるレーザ記録媒体の多重記録の1例を示す断面概略図、第4図は本発明によるレーザ記録媒体の光吸収剤層の番号とパワー密度との関係を示すグラフ、そして第5図は本発明によるレーザ記録媒体の他の1例を示す断面概略図である。

11、13、22、23、30、32、34、51、53、54、55、56、：透明な薄膜、12、24、25、26、31、33、52、57 ：光吸収剤層、14、21、35、50 ：基板、27、28、29、36、37 ：記録ピット、B ：書込用ビーム、L ：焦点レンズ。

第 1 図

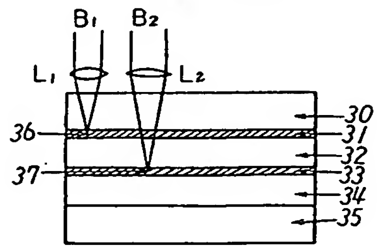


第 2 図



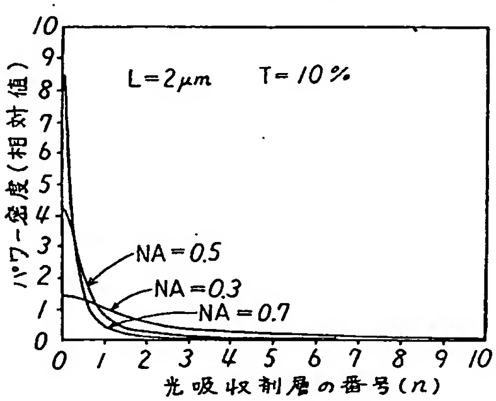
(A)　(B)　(C)

第 3 図



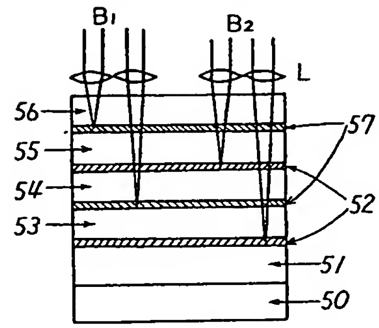
B1
B2
L1
L2
30
31
32
33
34
35
36
37

第 4 図



L=2μm T=10%
NA=0.5
NA=0.3
NA=0.7
パワー密度（相対値）
光吸収制層の番号（n）
0
1
2
3
4
5
6
7
8
9
10

第 5 図



B1
B2
L
56
55
54
53
57
52
51
50